VERIFICATION

The undersigned, of the below address, hereby certifies that he/she well knows both the English and Japanese languages, and that the attached is an accurate English translation of the PCT application filed on July 24, 2003 under No. PCT/JP03/09409.

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 19th day of January, 2004.

Signature:

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DESCRIPTION

GREASE COMPOSITION

Technical Field

[0001]

The present invention relates to a grease composition.

Background Art

[0002]

Grease is commonly used as a lubricant for mechanical parts such as constant velocity gears, transmission gears, ball bearings, roller bearings and the like.

[0003]

Most of the members composing such mechanical parts are made of metal, and friction between the metal members generates heat and wear at the sections of contact, resulting in a shorter life of the grease or of the mechanical parts themselves. Therefore, various additives such as friction reducers are included in lubricants to reduce the friction between metals.

[0004]

In recent years, however, the higher performance and lighter weights of such mechanical parts have resulted in restrictions on the conditions for their use, and friction due to contact between the metals occurs more frequently. With these types of mechanical

parts, it is often not possible to achieve an adequate friction-reducing effect even when using conventional greases containing added friction reducers.

[0005]

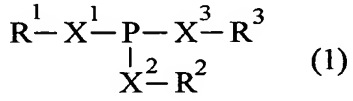
In addition, grease-filled mechanical parts are more frequently being used at ever higher temperatures, and therefore a grease which can provide a high friction-reducing effect even at high temperatures has been strongly desired.

[0006]

The present invention has been accomplished in light of these circumstances of the prior art, and its object is to provide a grease composition which can exhibit a high friction-reducing effect even at high temperatures.

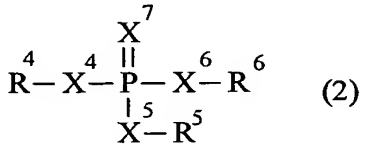
[0007]

In order to achieve this object, the grease composition of the invention is characterized by comprising a lubricating base oil combined with (A) 2-30 wt% of a thickener and (B) 0.1-10 wt% of at least one type of compound selected from the group consisting of phosphorus compounds represented by general formulas (1) and (2) below and their metal salts or amine salts, based on the total weight of the composition.



(1)

[wherein X^1, X^2 and X^3 may be the same or different and each represents an oxygen atom or sulfur atom, with at least two from among X^1, X^2 and X^3 being oxygen atoms, and R^1, R^2 and R^3 may be the same or different and each represents hydrogen or a C1-30 hydrocarbon group]



(2)

[wherein X^4, X^5, X^6 and X^7 may be the same or different and each represents an oxygen atom or sulfur atom, with at least three from among X^4, X^5, X^6 and X^7 being oxygen atoms, and R^4, R^5 and R^6 may be the same or different and each represents hydrogen or a C1-30 hydrocarbon group].

[0008]

According to the invention, combining a lubricating base oil with (A) a thickener and (B) at least one type of compound selected from the group consisting of phosphorus compounds represented by general formulas (1) and (2) above and their metal salts or amine salts in prescribed amounts yields a grease composition having a sufficiently high friction-reducing effect, and maintaining the high friction-reducing effect even at high temperature. Thus, even with increased speeds and lighter weights of mechanical parts such as constant velocity gears, or the use of

such mechanical parts at high temperatures, it is possible to prevent heat generation and wear due to friction between metals, to achieve satisfactorily lengthening of the usable life of grease and mechanical parts.

[0009]

The grease composition of the invention preferably further comprises an organic molybdenum compound.

[0010]

The (A) thickener in the grease composition of the invention is preferably lithium soap.

[0011]

Alternatively, the (A) thickener in the grease composition of the invention is preferably a urea-based thickener, and more preferably a urea-based thickener represented by the following general formula (3).

$$A\text{-}CONH\text{-}R^7\text{-}NHCO\text{-}B \quad (3)$$

[wherein A and B may be the same or different and each is a group represented by $-NHR^8$, $-NR^9R^{10}$ or $-OR^{11}$ (where R^8, R^9, R^{10} and R^{11} may be the same or different and each represents a C6-20 hydrocarbon group), and R^7 is a divalent hydrocarbon group].

[0012]

The grease composition of the invention preferably comprises at least one compound selected from among compounds represented by general formula (1) wherein X^1,

X^2 and X^3 are all oxygen atoms and compounds represented by general formula (2) wherein X^4, X^5, X^6 and X^7 are all oxygen atoms. In this case, component (B) may include both a compound wherein X^1-X^7 are all oxygen atoms and a compound wherein one from among X^1-X^7 is a sulfur atom while the others are oxygen atoms, but component (B) is preferably composed of only a compound wherein X^1-X^7 are all oxygen atoms.

Brief Description of the Drawings

[0013]

Figs. 1A and 1B are a perspective view and top view, respectively, of a test strip used for a friction test.

Best Mode for Carrying Out the Invention

[0014]

Preferred embodiments of the present invention will now be explained in detail.

[0015]

As lubricating base oils to be used in the grease composition of the invention there may be mentioned mineral oils and/or synthetic oils.

[0016]

Mineral oils include, for example, those obtained by methods commonly employed in lubricating oil production processes for petroleum refining, and more specifically, there may be mentioned oils obtained by

ordinary pressure distillation or reduced pressure distillation of crude oil, followed by purification of the lubricating oil fraction by oil deasphalting, solvent extraction, hydrogenating decomposition, solvent dewaxing, catalytic dewaxing, hydrogenation refining, sulfuric acid washing, clay refining and the like.

[0017]

As specific examples of synthetic oils there may be mentioned poly α-olefins such as polybutene, 1-octene oligomer and 1-decene oligomer or their hydrogenated forms; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate and di-3-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate and pentaerythritol pelargonate; alkylnaphthalenes,; alkylbenzenes; polyoxyalkylene glycols; polyphenyl ethers; dialkyldiphenyl ethers; silicone oils; and mixtures thereof.

[0018]

The dynamic viscosity of these lubricating base oils at 100°C is preferably 2-40 mm^2/s and more preferably 3-20 mm^2/s. The viscosity index of the base oil used is preferably 90 or greater and more preferably 100 or greater.

[0019]

According to the invention, the aforementioned lubricating base oil is combined with (A) a thickener and (B) at least one type of compound selected from the group consisting of phosphorus compounds represented by general formulas (1) and (2) above and their metal salts or amine salts in prescribed amounts. Hereunder, these components will sometimes be referred to as component (A) and component (B).

[0020]

There are no particular restrictions on the (A) thickener, but soap-based thickeners, for example, are preferably used. Using a soap-based thickener can increase the effect of preventing damage to mechanical parts.

[0021]

As specific examples of soap-based thickeners there may be mentioned sodium soaps, calcium soaps, aluminum soaps and lithium soaps, but lithium soaps are preferred among these from the standpoint of moisture resistance and thermal stability. As examples of lithium soaps there may be mentioned lithium stearate and lithium-12-hydroxystearate.

[0022]

Preferred examples for the (A) thickener are urea-based thickeners. Using a urea-based thickener can

increase the effect of preventing damage to mechanical parts.

[0023]

As examples of urea-based thickeners there may be mentioned urea compounds such as diurea compounds, triurea compounds, tetraurea compounds and polyurea compounds (other than diurea compounds, triurea compounds and tetraurea compounds), urethane compounds such as urea-urethane compounds and diurethane compounds, and mixtures thereof. Preferred among these are diurea compounds, urea-urethane compounds, diurethane compounds and mixtures thereof.

[0024]

Preferred examples of urea-based thickeners are those represented by the following general formula (3).

$$A\text{-}CONH\text{-}R^7\text{-}NHCO\text{-}B \quad (3)$$

The compounds represented by general formula (3) include diurea compounds, urea-urethane compounds and diurethane compounds.

[0025]

In formula (3), A and B may be the same or different and each is a group represented by $-NHR^8$, $-NR^9R^{10}$ or $-OR^{11}$. Here, R^8, R^9, R^{10} and R^{11} may be the same or different and each represents a C6-20 hydrocarbon group.

[0026]

As examples of hydrocarbon groups represented by R^8, R^9, R^{10} and R^{11} there may be mentioned straight-chain or branched alkyl, straight-chain or branched alkenyl, cycloalkyl, alkylcycloalkyl, aryl, alkylaryl and arylalkyl. More specifically there may be mentioned straight-chain or branched alkyl groups such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl; straight-chain or branched alkenyl groups such as hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl and eicosenyl; cyclohexyl groups; alkylcyclohexyl groups such as methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, diethylcyclohexyl, propylcyclohexyl, isopropylcyclohexyl, 1-methyl-3-propylcyclohexyl, butylcyclohexyl, amylcyclohexyl, amylmethylcyclohexyl, hexylcyclohexyl, heptylcyclohexyl, octylcyclohexyl, nonylcyclohexyl, decylcyclohexyl, undecylcyclohexyl, dodecylcyclohexyl, tridecylcyclohexyl and tetradecylcyclohexyl; aryl groups such as phenyl and naphthyl; alkylaryl groups such as toluyl, ethylphenyl, xylyl, propylphenyl, cumenyl, methylnaphthyl, ethylnaphthyl, dimethylnaphthyl and propylnaphthyl; and arylalkyl groups such as benzyl, methylbenzyl and ethylbenzyl,

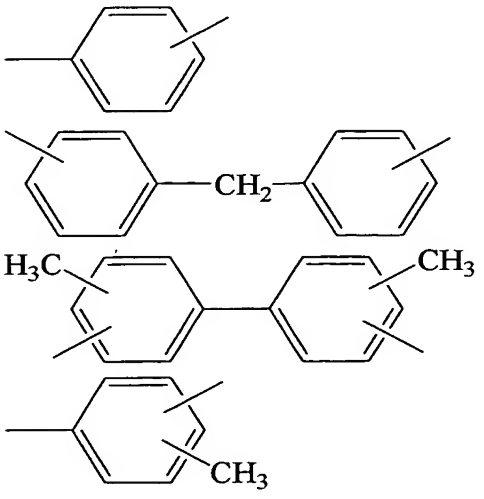
among which cyclohexyl, octadecyl and toluyl groups are particularly preferred.

[0027]

R^7 in formula (3) is a divalent hydrocarbon group. As specific divalent hydrocarbon groups there may be mentioned straight-chain or branched alkylene groups and straight-chain or branched alkenylene, cycloalkylene, arylene, alkylarylene and arylalkylene groups. The number of carbon atoms of the divalent hydrocarbon group represented by R^7 is preferably 6-20 and more preferably 6-15.

[0028]

As preferred examples of divalent hydrocarbon groups represented by R^7 there may be mentioned ethylene, 2,2-dimethyl-4-methylhexylene and groups represented by the following formulas (4) to (13), among which groups represented by formulas (5) and (7) are preferred.



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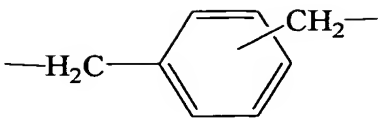

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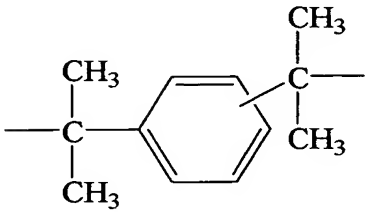

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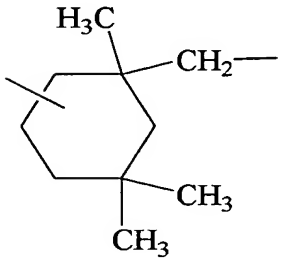

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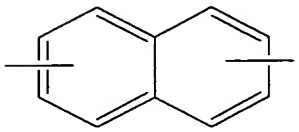

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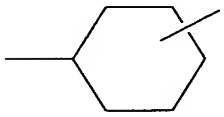

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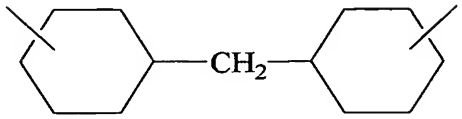


(13)

[0029]

The compounds represented by formula (3) may be obtained, for example, by reacting a diisocyanate represented by OCN-R^7-NCO with a compound represented by R^8NH_2, $R^9R^{10}NH$ or $R^{11}OH$ or a mixture thereof in the base oil at 10-200°C. R^7, R^8, R^9, R^{10} and R^{11} in the formulas for the raw material compounds have the same respective definitions as R^7, R^8, R^9, R^{10} and R^{11} in formula (3).

[0030]

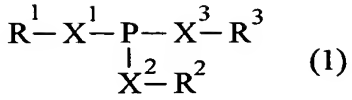
Bentone, silica gel or the like may be used as the (A) thickener.

[0031]

The content of component (A) in the grease composition of the invention is 2-30 wt% based on the total weight of the composition. If the content of the thickener is less than 2 wt%, the effect of adding the thickener will be insufficient, producing a less than satisfactory grease condition of the grease composition. For the same reason, the content of component (A) is preferably at least 5 wt% and more preferably at least 10 wt% based on the total composition. If the content of component (A) is greater than 30 wt%, the grease composition will become too hard and will fail to exhibit sufficient lubricating performance. For the same reason, the thickener content is preferably no greater than 25 wt% and more preferably no greater than 20 wt% based on the total composition.

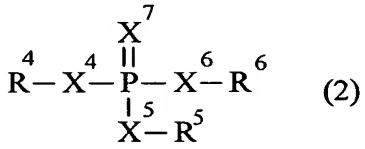
[0032]

Component (B) of the grease composition of the invention is at least one type of compound selected from the group consisting of phosphorus compounds represented by general formulas (1) and (2) below and their metal salts or amine salts.



(1)

[wherein X^1, X^2 and X^3 may be the same or different and each represents an oxygen atom or sulfur atom, with at least two from among X^1, X^2 and X^3 being oxygen atoms, and R^1, R^2 and R^3 may be the same or different and each represents hydrogen or a C1-30 hydrocarbon group]



(2)

[wherein X^4, X^5, X^6 and X^7 may be the same or different and each represents an oxygen atom or sulfur atom, with at least three from among X^4, X^5, X^6 and X^7 being oxygen atoms, and R^4, R^5 and R^6 may be the same or different and each represents hydrogen or a C1-30 hydrocarbon group].

[0033]

As specific C1-30 hydrocarbon groups represented by R^1 to R^6 there may be mentioned alkyl, cycloalkyl, alkenyl, alkylcycloalkyl, aryl, alkylaryl and arylalkyl.

[0034]

As examples of the aforementioned alkyl groups there may be mentioned alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl (which

alkyl groups may be either straight-chain or branched).

[0035]

As examples of the aforementioned cycloalkyl groups there may be mentioned C5-7 cycloalkyl groups such as cyclopentyl, cyclohexyl and cycloheptyl. As examples of the aforementioned alkylcycloalkyl groups there may be mentioned C6-11 alkylcycloalkyl groups such as methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methylethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl and diethylcycloheptyl (with any desired position of substitution of the alkyl groups on the cycloalkyl groups).

[0036]

As examples of the aforementioned alkenyl groups there may be mentioned alkenyl groups such as butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl and octadecenyl (which alkenyl groups may be either straight-chain or branched, and the double bond may be at any desired position).

[0037]

As examples of the aforementioned aryl groups

there may be mentioned aryl groups such as phenyl and naphthyl. As examples of the aforementioned alkylaryl groups there may be mentioned C7-18 alkylaryl groups such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl and dodecylphenyl (which alkyl groups may be either straight-chain or branched, with any desired position of substitution on the aryl groups).

[0038]

As examples of the aforementioned arylalkyl groups there may be mentioned C7-12 arylalkyl groups such as benzyl, phenylethyl, phenylpropyl, phenylbutyl, phenylpentyl and phenylhexyl (wherein the alkyl groups may be either straight-chain or branched).

[0039]

The C1-30 hydrocarbon groups represented by R^1 to R^6 are preferably C1-30 alkyl groups or C6-24 aryl groups, more preferably C3-18 alkyl groups, and even more preferably C4-12 alkyl groups.

[0040]

R^1, R^2 and R^3 may be the same or different and each represents hydrogen or one of the aforementioned hydrocarbon groups, with preferably 1 to 3, more preferably 1-2 and even more preferably 2 from among R^1, R^2 and R^3 being the aforementioned hydrocarbon groups.

[0041]

Also, R^4, R^5 and R^6 may be the same or different and each represents hydrogen or one of the aforementioned hydrocarbon groups, with preferably 1 to 3, more preferably 1 or 2 and even more preferably 2 from among R^4, R^5 and R^6 being the aforementioned hydrocarbon groups.

[0042]

In the phosphorus compounds represented by general formula (1), at least two from among X^1 to X^3 must be oxygen atoms, but preferably all of X^1 to X^3 are oxygen atoms.

[0043]

In the phosphorus compounds represented by general formula (2), at least three from among X^4 to X^7 must be oxygen atoms, but preferably all of X^4 to X^7 are oxygen atoms.

[0044]

As examples of phosphorus compounds represented by general formula (1) there may be mentioned phosphorous acid and monothiophosphorous acid; phosphorous acid monoesters and monothiophosphorous acid monoesters having one of the aforementioned C1-30 hydrocarbon groups; phosphorous acid diesters and monothiophosphorous acid diesters having two of the aforementioned C1-30 hydrocarbon groups; phosphorous

acid triesters and monothiophosphorous acid triesters having three of the aforementioned C1-30 hydrocarbon groups; and mixtures thereof. Preferred among these are phosphorous acid monoesters and phosphorous acid diesters, with phosphorous acid diesters being more preferred.

[0045]

As examples of phosphorus compounds represented by general formula (2) there may be mentioned phosphoric acid and monothiophosphoric acid; phosphoric acid monoesters and monothiophosphoric acid monoesters having one of the aforementioned C1-30 hydrocarbon groups; phosphoric acid diesters and monothiophosphoric acid diesters having two of the aforementioned C1-30 hydrocarbon groups; phosphoric acid triesters and monothiophosphoric acid triesters having three of the aforementioned C1-30 hydrocarbon groups; and mixtures thereof. Preferred among these are phosphoric acid monoesters and phosphoric acid diesters, with phosphoric acid diesters being more preferred.

[0046]

As salts of the phosphorus compounds represented by general formula (1) and (2) there may be mentioned salts having all or a portion of the acidic hydrogens of the phosphorus compound neutralized. Such phosphorus compound salts may be obtained by reacting

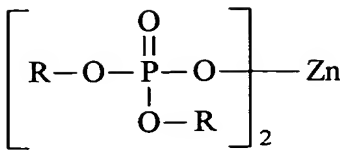
phosphorus compounds with metal bases such as metal oxides, metal hydroxides, metal carbonates and metal chlorides, or nitrogen compounds such as ammonia or amine compounds having only C1-30 hydrocarbon groups or hydroxyl group-containing hydrocarbon groups in the molecule.

[0047]

As metals for these metal bases there may be mentioned, specifically, alkali metals such as lithium, sodium, potassium and cesium, alkaline earth metals such as calcium, magnesium and barium, and heavy metals such as zinc, copper, iron, lead, nickel, silver and manganese. Preferred among these are alkaline earth metals such as calcium and magnesium, and zinc.

[0048]

The aforementioned phosphorus compound metal salts differ in structure depending on the valence of the metals and the numbers of OH groups or SH groups in the phosphorus compounds, and therefore no restrictions are placed on the structure. For example, when 1 mole of zinc oxide is reacted with 2 moles of a phosphoric acid diester (one OH group), a compound having the structure represented by formula (14) below may be obtained as the major product, although it may also be obtained as a polymerized molecule.



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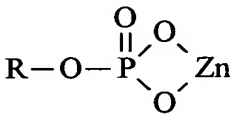
[0049]

As another example, 1 mole of zinc oxide may be reacted with 1 mole of a phosphoric monoester (two OH groups) to obtain a compound having the structure represented by formula (15) below as the major product, although it may also be obtained as a polymerized molecule.



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[0050]

As examples of the aforementioned nitrogen compounds there may be mentioned ammonia, monoamines, diamines, polyamines and the like. Specific examples include alkylamines with C1-30 alkyl groups such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine,

diundecylamine, didodecylamine, ditridecylamine, ditetradecylamine, dipentadecylamine, dihexadecylamine, diheptadecylamine, dioctadecylamine, methylethylamine, methylpropylamine, methylbutylamine, ethylpropylamine, ethylbutylamine and propylbutylamine (wherein the alkyl groups may be either straight-chain or branched);

[0051]

alkenylamines with C2-30 alkenyl groups such as ethenylamine, propenylamine, butenylamine, octenylamine and oleylamine (wherein the alkenyl groups may be either straight-chain or branched); alkanolamines having C1-30 alkanol groups such as methanolamine, ethanolamine, propanolamine, butanolamine, pentanolamine, hexanolamine, heptanolamine, octanolamine, nonanolamine, methanolethanolamine, methanolpropanolamine, methanolbutanolamine, ethanolpropanolamine, ethanolbutanolamine and propanolbutanolamine (wherein the alkanol groups may be either straight-chain or branched);

[0052]

alkylenediamines having C1-30 alkylene groups such as methylenediamine, ethylenediamine, propylenediamine and butylenediamine; polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine; compounds having C8-20 alkyl groups or alkenyl groups

on the aforementioned monoamines, diamines or polyamines, such as undecyldiethylamine, undecyldiethanolamine, dodecyldipropanolamine, oleyldiethanolamine, oleylpropylenediamine and stearyltetraethylenepentamine, or heterocyclic compounds such as N-hydroxyethyloleylimidazoline; alkylene oxide adducts of these compounds; and mixtures thereof.

[0053]

Preferred among these nitrogen compounds are aliphatic amines (either straight-chain or branched) having C10-20 alkyl groups or alkenyl groups, such as decylamines, dodecylamines, tridecylamines, heptadecylamines, octadecylamines, oleylamines and stearylamines.

[0054]

According to the invention, component (B) is preferably a metal salt or amine salt of a phosphorus compound represented by general formula (1) or (2) above, and it is more preferably a metal salt of the phosphorus compound. Using such compounds as component (B) will tend to produce a greater friction-reducing effect.

[0055]

From the standpoint of thermal stability there are preferred phosphorus compounds represented by general

formula (2) and their salts.

[0056]

The compounds for component (B) may be used alone or in combinations of two or more.

[0057]

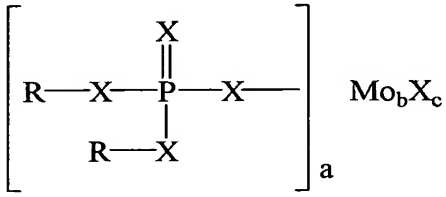
The content of component (B) is 0.1-10 wt% based on the total composition. If the content of component (B) is less than 0.1 wt%, the friction-reducing effect will be insufficient, and reduction of friction between metal members of mechanical parts will be impossible to achieve especially at high temperature. For the same reason, the content of component (B) is preferably 0.3 wt% or greater and more preferably 0.5 wt% or greater based on the total composition. If the content of component (B) exceeds 10 wt%, no commensurate improvement in the friction-reducing effect will be achieved. For the same reason, the content of component (B) is preferably no greater than 7 wt% and more preferably no greater than 5 wt% based on the total composition.

[0058]

The grease composition of the invention comprises component (A) and component (B) described above added to the lubricating base oil, but it may also contain an organic molybdenum compound in addition to these components.

[0059]

As examples of organic molybdenum compounds to be used for the invention there may be mentioned the phosphoric acid or thiophosphoric acid ester derivatives represented by general formula (16) below, and the dithiocarbamic acid ester derivatives represented by general formula (17) below.



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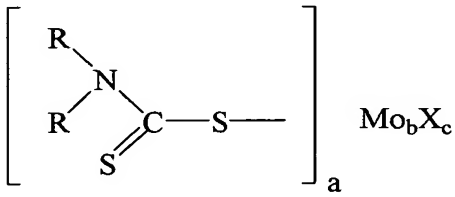


(17)

[0060]

In general formulas (16) and (17), each R may be the same or different and represents a C1 or greater hydrocarbon group, the c number of X groups may be the same or different with each representing an oxygen or sulfur atom, and a, b and c each represent integers of 1-6.

[0061]

As examples of hydrocarbon groups represented by R in formulas (16) and (17) above there may be mentioned C1-24 alkyl groups, C5-7 cycloalkyl groups, C6-11

alkylcycloalkyl groups, C6-18 aryl groups, C7-24 alkylaryl groups and C7-12 arylalkyl groups.

[0062]

As the aforementioned alkyl groups there may be mentioned, specifically, methyl, ethyl, propyl (including all branched isomers), butyl (including all branched isomers), pentyl (including all branched isomers), hexyl (including all branched isomers), heptyl (including all branched isomers), octyl (including all branched isomers), nonyl (including all branched isomers), decyl (including all branched isomers), undecyl (including all branched isomers), dodecyl (including all branched isomers), tridecyl (including all branched isomers), tetradecyl (including all branched isomers), pentadecyl (including all branched isomers), hexadecyl (including all branched isomers), heptadecyl (including all branched isomers), octadecyl (including all branched isomers), nonadecyl (including all branched isomers), eicosyl (including all branched isomers), heneicosyl (including all branched isomers), docosyl (including all branched isomers), tricosyl (including all branched isomers) and tetracosyl (including all branched isomers).

[0063]

As the aforementioned cycloalkyl groups there may be mentioned, specifically, cyclopentyl, cyclohexyl and

cycloheptyl.

[0064]

As the aforementioned alkylcycloalkyl groups there may be mentioned, specifically, methylcyclopentyl (including all substitution isomers), ethylcyclopentyl (including all substitution isomers), dimethylcyclopentyl (including all substitution isomers), propylcyclopentyl (including all branched isomers, substitution isomers), methylethylcyclopentyl (including all substitution isomers), trimethylcyclopentyl (including all substitution isomers), butylcyclopentyl (including all branched isomers, substitution isomers), methylpropylcyclopentyl (including all branched isomers, substitution isomers), diethylcyclopentyl (including all substitution isomers), dimethylethylcyclopentyl (including all substitution isomers), methylcyclohexyl (including all substitution isomers), ethylcyclohexyl (including all substitution isomers), dimethylcyclohexyl (including all substitution isomers), propylcyclohexyl (including all branched isomers, substitution isomers), methylethylcyclohexyl (including all substitution isomers), trimethylcyclohexyl (including all substitution isomers), butylcyclohexyl (including all branched isomers, substitution isomers), methylpropylcyclohexyl (including all branched isomers,

substitution isomers), diethylcyclohexyl (including all substitution isomers), dimethylethylcyclohexyl (including all substitution isomers), methylcycloheptyl (including all substitution isomers), ethylcycloheptyl (including all substitution isomers), dimethylcycloheptyl (including all substitution isomers), propylcycloheptyl (including all branched isomers, substitution isomers), methylethylcycloheptyl (including all substitution isomers), trimethylcycloheptyl (including all substitution isomers), butylcycloheptyl (including all branched isomers, substitution isomers), methylpropylcycloheptyl (including all branched isomers, substitution isomers), diethylcycloheptyl (including all substitution isomers) and dimethylethylcycloheptyl (including all substitution isomers).

[0065]

As the aforementioned aryl groups there may be mentioned, specifically, phenyl and naphthyl.

[0066]

As the aforementioned alkylaryl groups there may be mentioned, specifically, tolyl (including all substitution isomers), xylyl (including all substitution isomers), ethylphenyl (including all substitution isomers), propylphenyl (including all branched isomers, substitution isomers),

methylethylphenyl (including all substitution isomers), trimethylphenyl (including all substitution isomers), butylphenyl (including all branched isomers, substitution isomers), methylpropylphenyl (including all branched isomers, substitution isomers), diethylphenyl (including all substitution isomers), dimethylethylphenyl (including all substitution isomers), pentylphenyl (including all branched isomers, substitution isomers), hexylphenyl (including all branched isomers, substitution isomers), heptylphenyl (including all branched isomers, substitution isomers), octylphenyl (including all branched isomers, substitution isomers), nonylphenyl (including all branched isomers, substitution isomers), decylphenyl (including all branched isomers, substitution isomers), undecylphenyl (including all branched isomers, substitution isomers), dodecylphenyl (including all branched isomers, substitution isomers), tridecylphenyl (including all branched isomers, substitution isomers), tetradecylphenyl (including all branched isomers, substitution isomers), pentadecylphenyl (including all branched isomers, substitution isomers), hexadecylphenyl (including all branched isomers, substitution isomers), heptadecylphenyl (including all branched isomers, substitution isomers) and octadecylphenyl (including all branched isomers,

substitution isomers).

[0067]

As examples of the aforementioned arylalkyl groups there may be mentioned benzyl, phenethyl, phenylpropyl (including all branched isomers) and phenylbutyl (including all branched isomers).

[0068]

As compounds represented by general formula (16) and (17) there may be mentioned, specifically, molybdenum phosphate, molybdenum thiophosphate, molybdenum dithiophosphate and molybdenum dithiocarbamate.

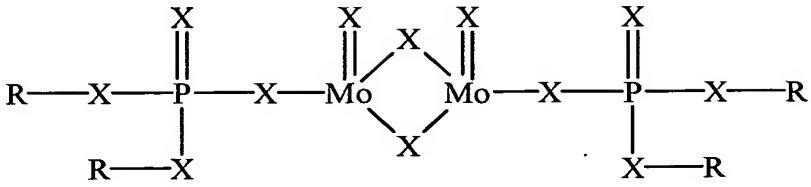
[0069]

The phosphoric acid or thiophosphoric acid ester derivatives represented by general formula (16) above and the dithiocarbamic acid ester derivatives represented by general formula (17) above are usually compounds obtained by reacting phosphoric acid esters, thiophosphoric acid esters or dithiocarbamic acid esters with inorganic molybdenum compounds (molybdenum trioxide, molbdenic acid or its salts, etc.), and if necessary together with a sulfur source.

[0070]

Molybdenum can take different valence states, and therefore the compounds obtained by the aforementioned reaction will usually be mixtures. The most typical

compounds are those represented by the following formulas (18) and (19).



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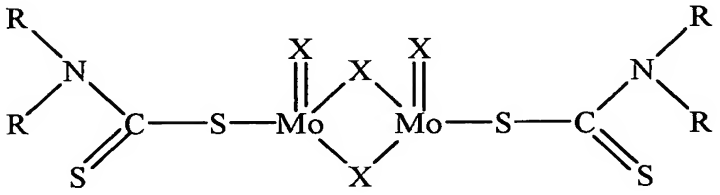

(19)

[0071]

According to the invention, the organic molybdenum compound used may be any one of the compounds represented by general formulas (16) and (17) above, or a mixture thereof, but from the standpoint of thermal stability it is preferably a compound represented by general formula (16). Addition of a compound represented by general formula (16) can provide excellent thermal stability particularly when the grease composition of the invention is used as bearing grease.

[0072]

The proportion of the organic molybdenum compound added is preferably at least 0.1 wt% and more preferably at least 0.5 wt% based on the total composition. If the proportion is less than 0.1 wt%,

the addition of the organic molybdenum compound will tend to yield no further friction-reducing effect. The proportion of the organic molybdenum compound added is also preferably no greater than 20 wt% and more preferably no greater than 10 wt% based on the total composition. If the proportion is greater than 20 wt%, there will tend to be no commensurate improvement in the friction-reducing effect.

[0073]

The grease composition of the invention may also contain, if necessary, solid lubricants, extreme pressure agents, antioxidants, oil agents, rust inhibitors, viscosity index improvers and the like to further enhance the performance, in a range which does not impair the properties.

[0074]

As specific solid lubricants there may be mentioned graphite, graphite fluoride, polytetrafluoroethylene, molybdenum disulfide, antimony sulfide, alkali (alkaline earth) metal borates and the like.

[0075]

As specific extreme pressure agents there may be mentioned organic zinc compounds such as zinc dialkyldithiophosphates, zinc diaryldithiophosphates, zinc dialkyldithiocarbamates and zinc

diaryldithiocarbamates, and sulfur-containing compounds such as dihydrocarbyl polysulfide, sulfidized esters, thiazole compounds and thiadiazole compounds.

[0076]

As specific antioxidants there may be mentioned phenol-based compounds such as 2,6-di-t-butylphenol and 2,6-di-t-butyl-p-cresol; amine-based compounds such as dialkyldiphenylamines, phenyl-α-naphthylamine and p-alkylphenyl-α-naphthylamines; sulfur-based compounds; and phenothiazine-based compounds.

[0077]

As specific oil agents there may be mentioned amines such as laurylamine, dimyristylamine, palmitylamine, stearylamine and oleylamine; higher alcohols such as lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol and oleyl alcohol; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid and oleic acid; fatty acid esters such as methyl laurate, methyl myristate, methyl palmitate, methyl palmitate, methyl stearate and methyl oleate; amides such as lauryl amide, myristyl amide, palmityl amide, stearyl amide and oleyl amide; fats and oils, and the like.

[0078]

As specific rust inhibitors there may be mentioned metal soaps; polyhydric alcohol partial esters such as

sorbitan fatty acid esters; amines; phosphoric acid; phosphoric acid salts, and the like.

[0079]

As specific viscosity index improvers there may be mentioned polymethacrylates, polyisobutylene, polystyrene, and the like.

[0080]

The grease composition of the invention may be obtained, for example, by adding component (A), component (B) and an organic molybdenum compound or other additives to a lubricating base oil, stirring the mixture, and passing it through a roll mill or the like. The grease composition of the invention may also be obtained by preadding the raw material of component (A) to the lubricating base oil and melting the mixture, stirring and mixing it to prepare component (A) in the lubricating base oil, and then further adding component (B) and an organic molybdenum compound or other additives, stirring the mixture and passing it through a roll mill or the like.

[0081]

The grease composition of the invention having the composition described above exhibits a sufficiently high friction-reducing effect, and the friction-reducing effect is maintained at a high level at high temperature. It is therefore highly useful as a gear

grease for constant velocity gears and transmission gears, as a bearing grease for ball bearings and roller bearings, and as an iron-manufacturing plant grease, and is particularly preferred as a grease for constant velocity joints, non-stage transmission bearings, and both automotive and railroad bearings.

[Examples]

[0082]

The present invention will now be explained in greater detail through examples and comparative examples, with the understanding that these examples are in no way limitative on the invention.

[Examples 1-12, Comparative Examples 1-24]

[0083]

Grease compositions were prepared according to the procedure described below, using a poly-α-olefin (dynamic viscosity at 40°C: 48 mm^2/s) in Examples 1-3, Comparative Examples 1-3 and Comparative Examples 13-15, and a mineral oil (dynamic viscosity at 40°C: 100 mm^2/s) in Examples 4-12, Comparative Examples 4-12 and Comparative Examples 16-24, as the lubricating base oil.

[0084]

In Examples 1-9, Comparative Examples 1-9 and Comparative Examples 13-21, diphenylmethane 4,4'-diisocyanate (MDI) was added to the lubricating base oil and heated to prepare a solution while

cyclohexylamine or additionally stearyl alcohol was added to the lubricating base oil and heated to prepare a solution, and the two solutions were combined so that the MDI, cyclohexylamine and stearyl alcohol were in the molar ratios shown in Tables 1-4. The additives listed below were then added to the produced gel-like substance in the contents shown in Tables 1-4, and the mixture was stirred and passed through a roll mill to obtain the desired grease composition.

[0085]

In Examples 10-12, Comparative Examples 10-12 and Comparative Examples 22-24, lithium 12-hydroxystearate was added to the lubricating base oil and heated to prepare a solution, and after cooling, the additives listed below were added in the contents shown in Tables 2-4. The mixture was then stirred and passed through a roll mill to obtain the desired grease composition.

Additives

ZnP: Zinc di(n-butyl)phosphate (phosphorus content: 13.2 wt%, sulfur content: 0%, zinc content: 13.0 wt%)

MoDTC: Molybdenum dioctyldithiocarbamate

MoDTP: Molybdenum dioctyldithiophosphate

ZnDTP: Zinc dipentyldithiophosphate

[0086]

[Friction test]

[0087]

The grease compositions of Examples 1-12 and Comparative Examples 1-24 were used for a friction test in the following manner.

[0088]

Figs. 1A and 1B are a perspective view and top view, respectively, of a test strip used for the friction test. As shown in these drawings, 1 g of the grease composition was filled into a needle holder 2 (14 mm x 10 mm x 2.5 mm) formed at the center of a lower disk 1 (φ24 mm x 7.9 mm), and then three needles (φ3 mm x 13.8 mm) were placed in the needle holder 2 and an upper disk 4 (φ20 mm x 13 mm) was situated thereover. Each of the test strips was set in an SRV friction testing machine in such a manner as to form an angle θ [deg] (the needle set angle) of 30 deg between line l_1 perpendicular to the sliding direction of the upper disk 4 through the center O on the upper surface of the lower disk 1 and line l_2 parallel to the lengthwise direction of the needle 3 through the center O. The two temperature conditions 80°C and 150°C were used in the testing machine, and the friction test was carried out at a frequency of 40 Hz, an amplitude of 3 mm and a load of 1000 N. The friction coefficients at 10 minutes after start of the test are shown in Tables 1-4.

TABLE 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Thickener	Raw material ratio [mol]	MDI	1	1	1	1	1	1	5	5	5
		Cyclohexylamine	2	2	2	2	2	2	8	8	8
		Stearyl alcohol	-	-	-	-	-	-	2	2	2
	Lithium 12-hydroxystearate		-	-	-	-	-	-	-	-	-
	Content [wt%]		15	15	15	15	15	15	8	8	8
Base oil	Mineral oil [wt%]		-	-	-	83	81	81	90	88	88
	PAO [wt%]		83	81	81	-	-	-	-	-	
Additives	ZnP [wt%]		2	2	2	2	2	2	2	2	2
	MoDTC [wt%]		-	2	-	-	2	-	-	2	-
	MoDTP [wt%]		-	-	2	-	-	2	-	-	2
Friction test	Friction coefficient	80°C	0.055	0.045	0.040	0.055	0.045	0.040	0.055	0.045	0.040
		150°C	0.055	0.045	0.045	0.055	0.045	0.045	0.055	0.045	0.045

TABLE 2

			Example 10	Example 11	Example 12	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Thickener	Raw material ratio [mol]	MDI	-	-	-	1	1	1	1	1	1
		Cyclohexylamine	-	-	-	2	2	2	2	2	2
		Stearyl alcohol	-	-	-	-	-	-	-	-	-
	Lithium 12-hydroxystearate		used	used	used	-	-	-	-	-	-
	Content [wt%]		10	10	10	15	15	15	15	15	15
Base oil	Mineral oil [wt%]		88	86	86	-	-	-	85	83	83
	PAO [wt%]		-	-	-	85	83	83	-	-	-
Additives	ZnP [wt%]		2	2	2	-	-	-	-	-	-
	MoDTC [wt%]		-	2	-	-	2	-	-	2	-
	MoDTP [wt%]		-	-	2	-	-	2	-	-	2
Friction test	Friction coefficient	80°C	0.055	0.045	0.040	0.180	0.050	0.055	0.190	0.050	0.055
		150°C	0.055	0.045	0.045	0.230	0.120	0.160	0.230	0.120	0.160

TABLE 3

			Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15
Thickener	Raw material ratio [mol]	MDI	5	5	5	-	-	-	1	1	1
		Cyclohexylamine	8	8	8	-	-	-	2	2	2
		Stearyl alcohol	2	2	2	-	-	-	-	-	-
	Lithium 12-hydroxystearate		-	-	-	used	used	used	-	-	-
	Content [wt%]		8	8	8	10	10	10	15	15	15
Base oil	Mineral oil [wt%]		92	90	90	90	88	88	-	-	-
	PAO [wt%]		-	-	-	-	-	-	83	81	81
Additives	ZnP [wt%]		-	-	-	-	-	-	-	-	-
	MoDTC [wt%]		-	2	-	-	2	-	-	2	-
	MoDTP [wt%]		-	-	2	-	-	2	-	-	2
	ZnDTP [wt%]		-	-	-	-	-	-	2	2	2
Friction test	Friction coefficient	80°C	0.185	0.050	0.055	0.180	0.055	0.055	0.050	0.045	0.040
		150°C	0.235	0.130	0.165	0.225	0.125	0.230	0.195	0.090	0.130

TABLE 4

			Comp. Ex. 16	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19	Comp. Ex. 20	Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24
Thickener	Raw material ratio [mol]	MDI	1	1	1	5	5	5	-	-	-
		Cyclohexylamine	2	2	2	8	8	8	-	-	-
		Stearyl alcohol	-	-	-	2	2	2	-	-	-
	Lithium 12-hydroxystearate		-	-	-	-	-	-	used	used	used
	Content [wt%]		15	15	15	8	8	8	10	10	10
Base oil	Mineral oil [wt%]		83	81	81	90	88	88	88	86	86
	PAO [wt%]		-	-	-	-	-	-	-	-	-
Additives	ZnP [wt%]		-	-	-	-	-	-	-	-	-
	MoDTC [wt%]		-	2	-	-	2	-	-	2	-
	MoDTP [wt%]		-	-	2	-	-	2	-	-	2
	ZnDTP [wt%]		2	2	2	2	2	2	2	2	2
Friction test	Friction coefficient	80°C	0.050	0.045	0.040	0.050	0.045	0.040	0.050	0.045	0.040
		150°C	0.190	0.085	0.130	0.185	0.090	0.135	0.190	0.085	0.135

[0089]

Tables 1 and 2 show that when the grease compositions of Examples 1-12 were used, a high friction-reducing effect was achieved as indicated by sufficiently low friction coefficients under both temperature conditions of 80°C and 150°C. When the grease compositions of Examples 2, 3, 5, 6, 8, 9, 11 and 12 were used, which further contained an organic molybdenum compound, it was possible to further increase the friction-reducing effect.

[0090]

When the grease compositions of Comparative Examples 1-24 were used, however, the friction coefficient was low especially at 150°C, and therefore the friction property was inadequate at high temperature.

Industrial Applicability

[0091]

As explained above, the present invention provides a grease composition exhibiting a sufficiently high friction-reducing effect, and the friction-reducing effect is maintained at a high level at high temperature. Thus, even with increased speeds and lighter weights of mechanical parts such as constant velocity gears, or the use of such mechanical parts at high temperatures, it is possible to prevent heat

generation and wear due to friction between metals, to achieve satisfactorily lengthening of the usable life of the grease and mechanical parts.